Research Article

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Synthesis and Characterization of Pure and Copper Doped HAp Nanoparticles by Microwave Irradiation Method

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ABSTRACT

Nanotechnology is an emerging concept in the field of science and technology. Hydroxyapatite (HAp) is a nano biomaterial incorporate as bone and teeth implants in the human body. In the present work, HAp was prepared using calcium hydroxide as a calcium source and orthophosphoric acid as a phosphorous source by chemical co-precipitation method associated with microwave irradiation method pure and copper doped Hap nanoparticles were synthesized by chemical co-precipitations method associated with microwave irradiation method. The prepared copper doped Hap was characterized by XRD, FTIR, SEM, EDAX, UV and PL techniques. The X-ray Diffraction (XRD) pattern reveals the crystalline size of the nanoparticles. The Fourier Transform Infrared Spectroscopy (FTIR) pattern gives the functional groups. Morphology and purity of sample were analysed by Scanning Electron Microscopy (SEM) and Energy Dispersion X-ray Diffraction (EDAX) analysis. The optical properties were carried out by using Ultra-Violet spectroscopy (UV) and Photo Luminance Spectroscopy(PL) analysis. The results are matches well with standard values.

Keywords: Crystalline size; Copper doped Hydroxyapatite; Co-preciptation method; Morphology; Optical Properties; Pure Hydroxyapatite**.**

1. INTRODUCTION

Nanotechnology is the study of extremely small structures, having a size of 0.1 to 100 nm. Nanomedicine is a relatively new field of science and technology. A brief explanation of various types of pharmaceutical nanosystems is given. Classification of nanomaterials based on their dimensions is given. An application of Nanotechnology in various fields such as health and medicine, electronics, energy and the environment are discussed in detail. Applications of nanoparticles in drug delivery, protein and peptide delivery, cancer are explained. Applications of various nanosystems in cancer therapy such as carbon nanotube, dendrimers, nanocrystal, nanowire, nanoshells etc. are given.

Calcium hydroxide has been included within several materials and antimicrobial formulations that are used in a number of treatment modalities in endodontics. Calcium hydroxide formulations are also used during the treatment of root perforations, root fractures and root resorption and have a role in dental traumatology. Phosphoric acid, also known as orthophosphoric acid, is a triprotic acid that exists as a dense liquid. It is an irritant or corrosive to the skin, eyes, and other mucous membranes of both humans and laboratory animals. Copper sulphate is an inorganic compound that combines sulphur with copper. It can kill bacteria, algae, roots, plants, snails, and fungi. The toxicity of copper sulphate depends on the copper content. Copper is an essential mineral.

In the present study, Copper doped Hap nanoparticles were used for the chemical synthesis of Cu HAp nanoparticles under different physical conditions. The synthesized Cu HAp nanoparticles were characterized SEM(Scanning Electron Microscopy), EDAX (Electron Dispersive X-Ray analysis), FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Diffraction), UV (UV-visible Spectroscopy), and PL (Photo Luminance Spectroscopy).

2. MATERIALS & METHODS

2.1 Preparation of Pure HAp Nanoparticles

The pure HAp nanoparticles were synthesized by the co-precipitation method. 3.705g of calcium hydroxide dissolved with 50ml of distilled water. 2.94g of orthophosphoric acid dissolved with 50ml of distilled water. Both solutions stirred for 30 min in separate beakers. After 30min orthophosphoric acid was added to the calcium hydroxide solution, the mixture was allowed to stirrer for 30min. The NaOH solution added drop by drop into the solution to maintained pH up to 12. Then the solution was stirred 30 min. After 30 min the solution

was ageing 1 day at room temperature. The settled precipitate was washed by distilled water and dried in a microwave oven at 75w for 20 min. The dried sample was grained in mortar. The mixture was kept in a muffle furnace at 4hrs.To get a white colour pure hydroxyapatite Nano powder.

2.2 Synthesis of Cu Hap Nanoparticles

The Cu doped HAp nanoparticles were synthesized by the co-precipitation method. 3.705g of calcium hydroxide dissolved in 50ml of distilled water. 2.94g of orthophosphoric acid dissolved in 50ml of distilled water.0.6242g of copper dissolved in 50ml of distilled water. These solutions were stirred for 30minutes in separate beakers. After 30min orthophosphoric acid assorted with calcium hydroxide solution, it was allowed to stir for 30minutes. Further, the Copper solution was added to the above mixture and allowed to stirred for 30 minutes. Then the NaOH solution added to maintain the pH up to 12. Then the solutions were agitated 30 minutes. After 30 min the solution was ageing for 1 day at room temperature. The water was removed and dried in the microwave oven at 75w for 20 minutes. The dried sample was grained in mortar. The mixture was kept in a muffle furnace at 4hrs. To get a Copper doped hydroxyapatite nanopowder.

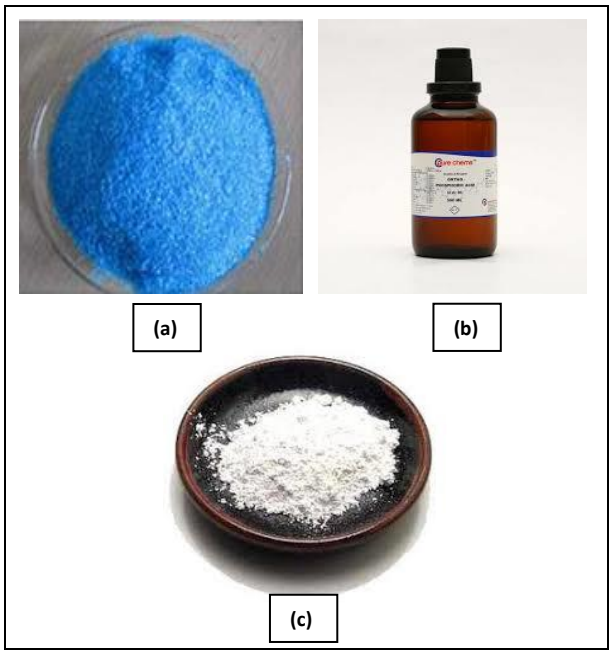

Fig. 1: (a) Copper Sulphate (b) Orthophosphoric Acid (c) Calcium Hydroxide

2.3 Characterization Techniques

2.3.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. The lattice parameter of the sample was calculated using the following equation:

$$1/d^2 = (4(h^2+hk+k^2)/3a)+(1^2/c^2))$$

Where d is the spacing between the planes, a and c are the lattice parameter. The unit cell volume (V) of the sample was described using the given equation:

$$V=(\sqrt{3}/2) +a^2+c^2$$

The average crystalline size of the sample was determined by using Scherer's formula.

$$D=K\lambda/\beta\cos\theta$$

Where, D denotes the average crystalline size of the sample, K represents the broadening constant, λ denotes the wavelength of CuKα radiation source ($1.54A^0$), β represents full width at half maximum, and an angle of diffraction is denoted by θ.

2.3.2 SEM and EDAX

The surface morphologies of synthesized Cu HAp samples were analysed using Scanning Electron Microscopic analysis (SEM). Energy dispersive spectroscopy is used to identify the elemental composition of the sample.

2.3.3 UV and PL

The emission of light or luminescence through this process is photoluminescence, PL. The absorption of light or luminescence through this process is UV-Visible Spectroscopy.

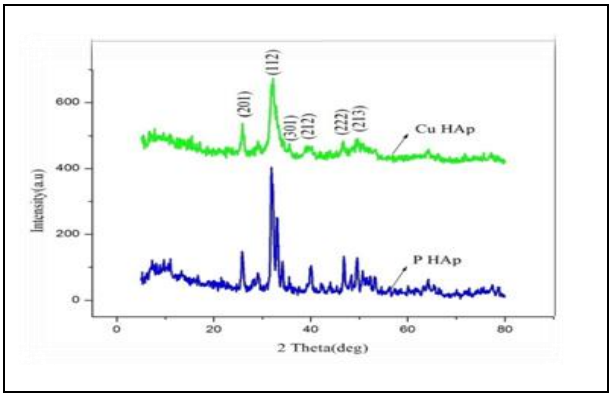

Fig. 2: XRD Analyses of Pure HAp and Cu HAp Nanoparticles

3. RESULTS

3.1 XRD Analysis

The XRD pattern of prepared pure Hap nanoparticles shown in fig. 2. The crystalline size of nanoparticles was determined from major the peak value. The average crystalline calculated by using the Debay-

Scherer formula is approximately in the range between 5-24nm.

3.2 SEM analysis

The morphological structure of the prepared nanocomposites was revealed in SEM. These analyses are useful in the crystalline structure, chemical composition and crystal orientations. Figure (a) shows Pure HAp nanoparticles, and figure (b) shows Copper doped HAp nanoparticles. Pure HAp nanoparticles cluster-like structure Copper doped HAp nanoparticles Cluster like structure but non-uniform. The formation of pure HAp is found to be 27.69 - 46.28 nm. The formation of Cu doped HAp is found to be 55.54 – 71.72 nm.

Table 1. XRD Analyses of Pure HAp and Cu HAp Nanoparticles

Sample Name	2theta (deg)	FWHM (deg)	D (A^0)	Intensity (counts)	Crystalline size(nm)	Average crystalline size(nm)	hkl	Lattice constant		Unit Volume
								A = b	c	
	25.84	0.5629	3.44	68	14.57		201			502.83
	31.97	0.7205	2.79	226	11.47		112			546.46
	35.97	0.3467	2.52	11	21.11		301			524.98
P HAp	39.10	0.4000	2.30	10	24.06	17.51	212	9.38	6.89	532.84
	42.25	0.4834	2.13	13	17.61		311			525.77
	46.81	0.5035	1.93	58	17.19		222			524.98
	49.50	0.5284	1.83	56	16.55		213			526.50
	25.87	0.92	3.44	35	8.80		201			504.27
	32.21	1.56	2.77	134	5.27		112			523.86
	35.00	1.20	2.53	15	6.95		301			512.87
CuHAp	39.55	1.90	2.27	18	4.39	7.91	212	9.35	6.86	511.63
	41.95	0.50	2.15	4	16.99		311			530.59
	46.65	1.10	1.94	22	7.86		222			530.23
	49.40	1.70	1.84	29	5.14		213			531.71

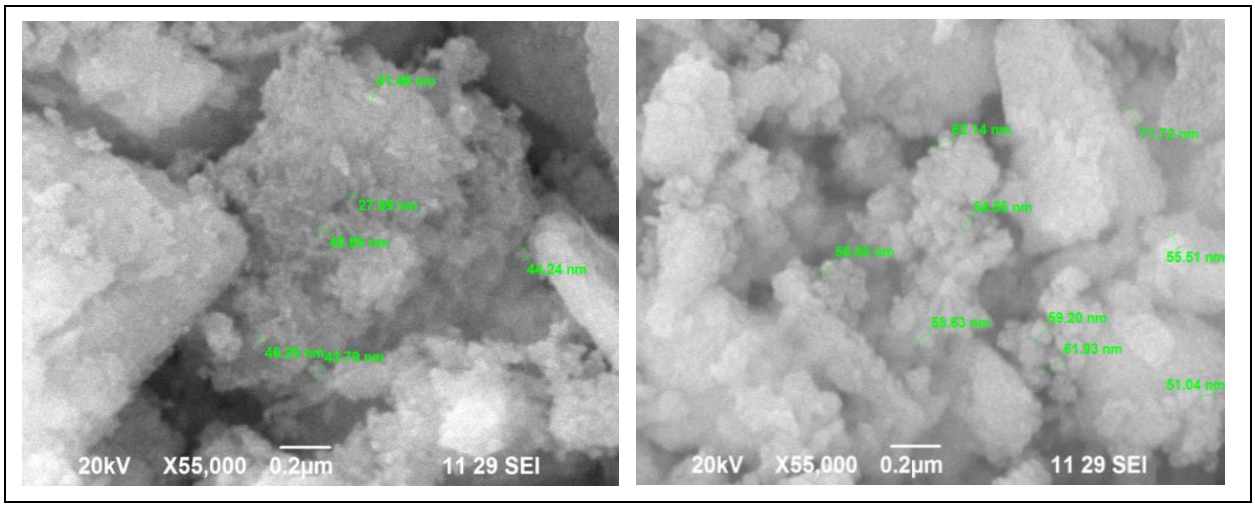

Fig. 3: SEM Image for Pure (a) and Cu Doped HAp(b) Nanoparticles

3.3 EDAX Analysis

EDAX study analyze used to chemical composition present in the sample. The EDAX analysis consists of spectra showing peak corresponding to the elements making up the true composition of the sample being analyzed elemental mapping of a sample, and image analysis.

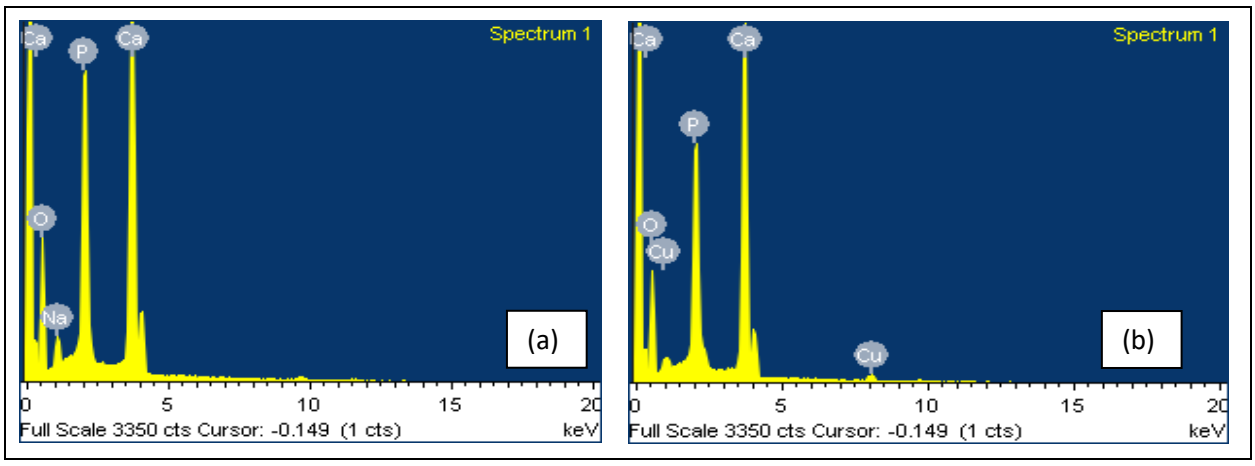

Fig. 4: EDAX Image for Pure and Cu Doped HAp Nanoparticles

Table 2. EDAX Analyses of Pure and Cu HAp Nanoparticles

Sample Name	Element	Weight %	Atomic %
P HAp	O K Na K P K Ca K	51.23 2.93 13.05 32.79	70.08 2.79 9.22 17.91
Cu HAp	O K P K Ca K Cu K	52.90 13.28 31.11 2.71	72.61 9.41 17.04 0.94

3.4 Fourier Transforms Infrared Spectroscopy (FTIR):

The characteristic bands present in the sample are predicted by the FTIR spectra. The presence of phosphate and hydroxyl groups is identified, which corresponds to HAp structure. The FTIR spectrum of HAp shows the vibration modes of phosphate at 870.70, 570.82 and 1044.26cm-1. Hydroxyl groups of HAp is revealed at 3454.85 cm-1 and 3744.12 cm-1 . The vibration modes at 569.86, 872.631 and 1043.31cm-1 reveal the presence of phosphate group and Hydroxyl groups at 3456.78 cm-1 and 3636.12 cm-1 for Cu HAp. Peaks at 1421.28 cm-1 and 1420.32 cm-1 represents the CH_3 stretching of carboxylic acid. The present groups were shown in table 3.3 and Fig 3.4

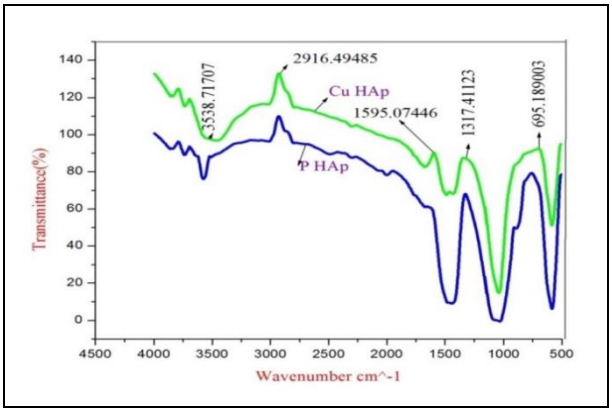

Fig. 5: FTIR Images of Pure HAp and Cu HAp Nanoparticles

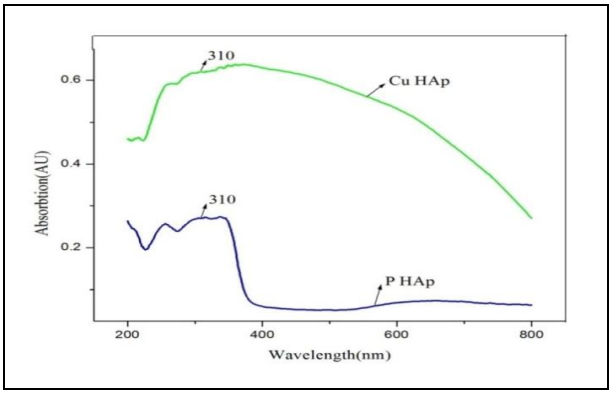

Fig: 6: UV-vis images of Pure HAp and Cu HAp Nanoparticles

Table 3. FTIR Analyses of Pure HAp and Cu HAp Nanoparticles

S.NO	Sample Name	Wave Number cm^{-1}				
		O-H stretching vibration	C-H stretching vibration	C=C stretching vibration	CH_3 stretching vibration	P-O Stretching vibration
1.	P HAp	3555.67	2918.55	1593.81	1319.58	694.84
2.	Cu HAp	3538.71	2916.49	1595.07	1317.41	695.18

Table 4. Band Gap Energy of Pure HAp and Cu HAp nanoparticles

S. No.	Sample Name	Wavelength (nm)	Bandgap energy(eV)
1.	Pure HAp	310	4.00
2.	Cu HAp	310	4.00

3.5 UV Analysis

UV–vis spectroscopy examines the sample's optical properties and bandgap energy. The wavelength spectrum of 310nm is present in the absorption spectra of HAp and Cu HAp nanoparticles. HAp and Cu HAp had a bandgap energy of 4.00eV. Due to quantum size effects and electronic structure changes, both samples have the same wavelength and bandgap energy. Table 3.4 shows the energy band and wavelength of the particles. The spectrum of HAp and Cu HAp was shown in Fig 3.5. And bandgap energy is shown in Table: 3.4

3.6 Photoluminescence spectroscopy

The intensity of emission radiations was absorbed by photoluminescence spectroscopy. The emission radiation of HAp and Cu HAp is shown in Fig: 3.6. The excitation wavelength occurs at the range of 228.34nm for both HAp and Cu HAp .The emission band of Cu HAp located at 310.9nm. In HAp, there was no shift present at the range. The standard bandgap energy of HAp around the range 3.45 eV to 5.40 eV, while the calculated bandgap energy of both the samples is 3.189 eV.

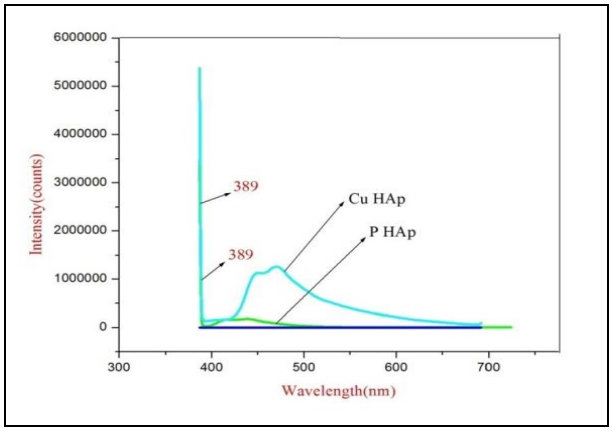

Fig. 7: PL analyses of pure HAp and Cu HAp Nanoparticles

4. CONCLUSION

Microwave irradiation was used to irradiate hydroxyapatite nanoparticles, which were green synthesized. The XRD pattern verified the sample's crystalline dimension, lattice parameter, and nanoparticle unit cell length. When comparing Cu HAp to HAp, the crystalline scale decreases. The existence of functional groups can be seen in the FTIR spectrum. It verifies the presence of phosphate and hydroxyl groups in the sample. UV research was used to determine the bandgap energy and wavelength. HAp and Cu HAp had a bandgap energy of 4.00eV. The morphological structure in a spherical shape is predicted by SEM research. The occurrence of calcium and phosphate groups in the ratio of 1.65 is confirmed by EDAX research. The sample's bandgap energy and optical absorption are shown by UV and PL analysis. The Bandgap energy measured was 4.00eV.

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